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(19)

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(54) PREPARATION OF FIBROUS SHEET PRODUCT

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to porous products and particularly to porous fibrous sheet products and to the preparation and uses therefor.

Porous sheet products are used in many locations in which the material of which the product is made needs to be inert to chemicals with which it comes into contact. 'Inert' as used herein means that the product is sufficiently inert to the environment to which it will be exposed during use to enable it to have a functional life. Typical examples of such products are electrolytic cell diaphragms, battery separators, fuel cell components, dialysis membranes and the like. Where the material of which they are made imparts the appropriate properties they may also be employed, say, to separate wetting from non-wetting fluids. Fluorinated polymers, and particularly polytetrafluoroethylene (PTFE), have been suggested as being suitable for the preparation of sheet products, and methods of making porous electrolytic cell diaphragms have been described for example in British Patent No. 1,081,046, and in British Patent No. 1,424,804.

The invention provides a method for preparing a porous fluorine-containing polymeric sheet product which method comprises the steps of introducing an electrically-conducting spinning liquid comprising a fluorine-containing polymeric material into an electric field whereby fibres are drawn from the liquid to an electrode and collecting the fibres so produced upon the electrode in the form of a sheet.

The process of electrotatic spinning involves the introduction of a suitable spinning liquid into an electric field whereby fibres are drawn from the liquid to an electrode. While being drawn from the liquid the fibres harden, which may involve mere cooling, for example where the liquid is normally solid at room temperature and is melted to enable spinning to take place, chemical hardening, for example by treatment with a hardening vapour or by cross-linking, or by evaporation of solvent, for example by dehydration. The resulting fibres may be collected on a suitably located receiver and subsequently stripped from it in the form of a sheet. Any of these techniques may be employed in the process of the invention, the selection of an appropriate technique depending inter alia, upon the polymer being spun. The fibres produced by the electrostatic spinning process are thin, usually of the order of 0.1 to 25 microns, preferably 0.5 to 10 microns, and more preferably 1 to 5 microns in diameter, and the process enables considerable control to be exercised, based largely upon experience, upon fibre diameter. The porosity of a fibrous sheet produced by this method depends to some extent upon the fibre diameter and some control of pore size may be exercised by selection of appropriate fibre diameter. For a given sheet density fibres of small diameter tend to give products having small pores, while those of greater diameter give larger pores. Preferred products have a pore size such that at least 80% of the pores are less than 5 μ in diameter. Examples of fluorine-containing polymeric materials include polyvinyl fluoride, polyvinylidene fluoride, polychlorotrifluoroethylene, fluorinated ethylene/propylene copolymers, perfluoroalkoxy compounds and fluorinated ethylene/perfluorovinyl ether copolymers. The preferred polymer is polytetrafluoroethylene.

The spinning liquid should contain the fluorine-containing polymeric material in such quantity that it is capable of forming a fibre

and the fibre which is formed should have cohesive properties such that the fibre form is retained during any post-fibreization treatment, for example hardening, until the fibre has hardened sufficiently not to lose its fibrous shape on detachment from a support.

The spinning liquid preferably comprises a dispersion of fluorine-containing polymeric material in a suitable liquid medium; conveniently the spinning liquid comprises also an additional component, for example a polyamine component, which acts to enhance the viscosity of the spinning liquid and to improve its fibre-forming properties. Most convenient for this purpose, we have found, is an organic polymeric material which subsequent to fibre formation can, if desired, be destroyed for example by sintering.

Where sheets are spun from dispersion they often have a tendency to be friable, being mere agglomerations of discrete particles of fluorine-containing polymeric material held together in the form of fibres by the additional organic polymeric component present. Preferably, therefore, such sheets are sintered so that the particles soften and flow into each other, and so that the fibres become point bonded without destroying the porous nature of the product. In the case of polytetrafluoroethylene sintering may conveniently be carried out between 330°C and 450°C, preferably between 370°C and 390°C. The sintering temperature preferably is sufficiently high to destroy completely any undesirable organic component in the final product e.g. emulsifying agent, or organic polymeric material added solely to enhance the viscosity of the spinning liquid.

The additional polymeric component need be employed only in a relatively small proportion, usually within the range 0.0001 to 12%, preferably 0.01 to 8%, and more preferably 0.1—4% by weight of the spinning liquid, although the precise concentration for any particular application can easily be determined by trial.

The degree of polymerisation of the additional polymeric component is preferably greater than about 2000 units linearly, and a wide range of such polymers is available. An important requirement is solubility of the polymeric component in the selected solvent or dispersing medium, which is preferably water. As examples of water-soluble polymeric components for this purpose we may mention polyethylene oxide, polyacrylamide, polyvinyl pyrrolidone and polyvinyl alcohol. Where an organic liquid is employed to prepare the spinning liquid, either as a sole liquid or as a component thereof, a further wide range of additional polymeric components is available, for example polystyrene and polymethylmethacrylate.

The degree of polymerisation of the additional polymeric component will be selected in the light of required solubility and the ability of the polymeric component to impart the desired properties of viscosity to the spinning liquid and cohesion to the fibre which is produced.

We have found that generally the viscosity of the spinning liquid whether due solely to the presence of fluorine-containing polymeric material or partly contributed to by the additional polymeric component or other ingredients, should be greater than 0.1 but not greater than 150 poise. Preferably it is between 0.5 and 50 poise and more preferably between 1 and 10 poise (viscosities being measured at low shear rates). the viscosity required, using a given additional polymeric component, will usually vary with the molecular weight of the APC component, the lower the molecular weight of the component the higher the final viscosity which is generally needed. Again, as the molecular weight of the additional polymeric component is increased a lower concentration of the component is required in the spinning liquid to give good fibreization. Thus, as examples we would mention that we have found that when using a polyethylene oxide of molecular weight 100,000 as additional polymeric component a concentration of about 12% by weight relative to the fluorine-containing polymeric material is needed to give satisfactory fibreization, whereas with a molecular weight of 300,000 a concentration of 1 to 6% may be adequate. Again, at a molecular weight of 600,000 a concentration of 0.5 to 4% is satisfactory, while at a molecular weight of 4×10^6 a concentration as low as 0.2% may give good fibreization.

The effect upon fibre diameter of varying the molecular weight and concentration of an additional polymeric component (polyethylene oxide) in a spinning liquid containing an aqueous dispersion of polytetrafluoroethylene of number average median particle size 0.22 microns (the Standard Specific Gravity of polymer by ASTM test D 792—50 being 2.190) containing 3.6% by weight, based on the weight of the dispersion, of surfactant "Triton" X100 (Rohm and Haas) and having a polytetrafluoroethylene content of 60% by weight is illustrated in the table below.

$\bar{M}$ n of polyethylene oxide	concentration of polyethylene oxide (weight % of total spinning liquid)	diameter of sintered fibres
2×10^5	4	1.0 – 1.6 μm
3×10^5	2	1.0 – 2.0 μm
4×10^5	2	1.2 – 2.8 μm
6×10^5	1	1.5 – 4.0 μm
4×10^6	0.2	1.5 – 4.5 μm

Increasing the concentration of a given molecular weight additional polymeric component does tend to broaden the fibre diameter range, but this is not usually undesirably excessive, particularly with lower molecular weight components. However, the concentration of additional polymeric component may markedly affect the morphology of the fibres obtained; the effect resulting from any particular combination of components and concentrations can be determined by simple trial.

Additional polymeric components other than polyethylene oxide e.g. polyvinyl alcohol and polyvinyl pyrrolidone may require the use of other concentrations, but the optimum can easily be determined for any given combination of components. For example with the above mentioned additional polymeric components we have found that concentrations greater than 6% w/w are required to give fibres which average between 0.5 and 1 micron in diameter. Selection of the component will be made with regard to its effect upon the properties of the final product, including colouration which may follow any sintering process which may be employed. Both polyvinyl alcohol and polyvinyl pyrollidone, we find, tend to give weaker products and also strong colouration after sintering compared with polyethylene oxide.

The concentration of the fluorine-containing polymeric material will depend upon the amount required to provide adequate fibre properties, and will be influenced also by the need to produce a liquid of appropriate viscosity and speed of fibre hardening. Thus in general we use a concentration of fluorine-containing polymeric material within the range 25% by weight to saturation (in the case of dispersion, 'saturation' means the maximum concentration of polymeric material which may be included without destroying the useful spinnability of the liquid) preferably 40 to 70% by weight, and more preferably 50 to 60% by weight.

It will be appreciated that the concentration of each of the components of the spinning liquid must be adjusted to take account of the presence and concentration of any other and their relative effects upon viscosity, etc.

The spinning liquid should have some electrical conductivity, although this may vary between quite wide limits, for example we prefer to employ spinning liquids having conductivity within the range 1×10^{-6} to 5×10^{-2} siemens cm^{-1}.

The incorporation of a small quantity of an electrolyte in the spinning liquid may be used to increase its conductivity. Thus, we find that the presence of a very small amount, e.g. 0.2—3%, usually about 1% of a salt by weight of spinning liquid generally suffices. For example an inorganic salt, e.g. KCl, added to a polytetrafluoroethylene dispersion increases the conductivity of the dispersion considerably (1% causes an increase in conductivity from 1.8×10^{-4} to 1.2×10^{-2} siemens cm^{-1}).

Dispersions having high conductivities tend to produce finer fibres than do less conducting dispersions. For example a dispersion having a conductivity of 1.8×10^{-4} siemens cm^{-1} gave, under certain conditions, fibres of diameters 2 to 3 microns whereas under the same conditions the same dispersion with the addition of 1% by weight of KCl gave fibres of only 0.5 to 1.5 micron in diameter. We found also that the fibres spread out over a wider and more even band on the collector electrode, although the total rate of production of fibre dropped somewhat.

Obviously the electrolyte selected for addition to the spinning liquid will be one which will have no adverse effect upon the product, either as a consequence of its presence in the spinning liquid or the final product, a wide range of salts capable of increasing conductivity are known.

Any convenient method may be employed to bring the spinning liquid into the electric field, for example we have supplied the spinning liquid to an appropriate position in the electric field by feeding it to a nozzle from which it is drawn by the field, whereupon fibreization occurs. Any suitable apparatus can be employed for this purpose; thus for example

we have fed the spinning liquid from a syringe reservoir to the tip of an earthed syringe needle, the tip being located at an appropriate distance from an electrostatically charged surface. Upon leaving the needle the fibres form between the needle tip and the charged surface.

Droplets of the spinning liquid may be introduced into the field in other ways which will be apparent to the skilled man, the only requirement being that they can be held within the field at a distance from the electrostatically charged surface such that fibreization occurs. For example they could be carried into the field on, say, a continuous carrier, e.g. a metal wire.

It will be appreciated that where the spinning liquid is fed into the field through a nozzle, several nozzles may be used to increase the rate of fibre production. Alternative means of bringing the spinning liquid into the field may be employed, for example a perforated plate may be employed, the perforations being fed with spinning liquid from a manifold.

In one embodiment which will be described for purposes of illustration only, the surface to which the fibres are drawn is a continuous surface, as of a drum, over which passes a belt which may be withdrawn from the region of charge, carrying with it the fibres which have been formed and which have become attached thereto. Such an arrangement is shown in the attached drawings in which Figure 1 is a diagrammatic side view of apparatus for the continuous production of fibres. In Figure 1, 1 is an earthed metal syringe needle supplied from a reservoir with spinning liquid at a rate related to the rate of fibre production. Belt 2 is of gauze driven by a driving roller 3 and passing over an idler roller 4 and to which is fed an electrostatic charge from a generator 5 (in the apparatus illustrated a Van de Graaff machine). Removal of the fibre mat 6 from belt 1 is by any convenient means, for example by suction or by air jet, or it may be removed by juxtaposition of a second belt carrying sufficient electrostatic charge to effect detachment of the mat from belt 2. In the Figure the mat is shown being picked up by a roller 7 rotating against the belt.

The optimum distance of the nozzle from the charged surface is determined quite simply by trial and error. We have found, for example, that using a charged surface with potential of the order of 20 Kv a distance of 10—25 cm is suitable, but as the charge, nozzle dimensions, liquid flow rate, charged surface area etc. are varied so the optimum distance may vary, and it is most conveniently determined by simple trial.

Alternative methods of fibre collection which may be employed include the use of a large rotating cylindrical charged collecting surface substantially as described, but the fibres being collected from another point on the surface by a non-electrically conducting pick-up means instead of being carried away on the belt. In a further embodiment the electrostatically charged surface may be the sides of a rotating tube, the tube being disposed coaxially with the nozzle and at an appropriate axial distance from it. Alternatively deposition of fibres and the formation of a tube may occur on a tubular or solid cylindrical former, with optionally subsequent removal of the fibrous sheet product from the former by any convenient means. The electrostatic potential employed will usually be within the range 5 Kv to 1000 Kv, conveniently 10—100 Kv and preferably 10—50 Kv. Any appropriate method of producing the desired potential may be employed. Thus, we illustrate the use of a conventional van de Graaff machine in Figure 1 but other commercially available and more convenient devices are known and may be suitable.

It is, of course, desirable that the electrostatic charge is not conducted from the charged surface and where the charged surface is contacted with ancillary equipment, for example a fibre collecting belt, the belt should be made of a non-conducting material (although it must not, of course, insulate the charged plate from the spinning liquid). We have found it convenient to use as the belt a thin Terylene net of mesh size 3mm ('Terylene' is a Registered Trade Mark of Imperial Chemical Industries Limited). Obviously all supporting means, bearings etc. for the equipment will be insulated as appropriate. Such precautions will be obvious to the skilled man.

Fibres having different properties may be obtained by adjusting their composition either by spinning a liquid containing a plurality of components, each of which may contribute a desired characteristic to the finished product, or by simultaneously spinning from different liquid sources fibres of different composition which are simultaneously deposited to form a sheet having an intimately intermingled mass of fibres of different material. A further alternative is to produce a sheet having a plurality of layers of different fibres (or fibres of the same material but with different characteristics e.g. diameter) deposited, say, by varying with time the fibres being deposited upon the receiving electrode. One way of effecting such variation, for example, would be to have a moving receiver passing in succession sets of spinnerets from which fibres are being electrostatically spun, said fibres being deposited in succession as the receiver reaches an appropriate location relative to the spinnerets.

To allow high production rates, hardening of the fibres should occur rapidly and where a solution or dispersion is used as the spinning liquid hardening is facilitated by the use of

a concentrated solution or dispersion so that the minimum of solvent or dispersing liquid has to be removed. It is preferred to use readily volatile solvents or dispersing liquids which may, for example be wholly or partly of a low boiling organic nature, and it is preferred to use relatively high temperatures in the vicinity of the fibres being formed. The use of a gaseous blast, usually air, particularly if the gas is warm, will often accelerate hardening of the fibre. Careful direction of the gaseous blast may also be used to cause the fibres, after detachment, to lay in a desired position or direction. However, using conditions as described in the Examples no particular precautions were needed to ensure rapid hardening. The preferred spinning conditions in air, are a temperature above 25°C (more preferably 30 to 50°C) and a humidity lower than 40%.

After their formation the fibres may be sintered at a temperature sufficiently high to destroy any undesirable organic component in the final product, e.g. material added solely to enhance viscosity.

Sintering is often accompanied by shrinkage; up to 65% reduction in area has been observed in a sheet consisting of 100% polytetrafluoroethylene fibres.

It is important, therefore, that the product is free to move during sintering so that shrinkage may occur evenly if so desired. We prefer to support the product, particularly if it is a flat sheet, in the horizontal position. Thus it may be supported upon a sheet of any material to which it does not stick, e.g. a fine gauze of stainless steel wire. However our preferred support is a bed of fine powder or particulate material which is stable at the sintering temperature. In particular we prefer to use as the support a bed comprising particles of a material the presence of which in the product will not be disadvantageous. For example, we have used a bed comprising titanium dioxide powder when preparing a wettable polytetrafluoroethylene sheet, since the presence of any titanium dioxide powder retained in the sheet will not be disadvantageous.

For many applications, especially where the porous sheet product is to be used as a diaphragm in an electrochemical cell, it is desirable or even essential that the product be capable of being wetted by a liquid, especially by a polar liquid, e.g. water. However polytetrafluoroethylene, for example, is not water wettable, and we have found it advantageous to incorporate in the product a material which imparts thereto a desired degree of water wettability.

According to another aspect of the invention, therefore, we provide a porous sheet product obtained by a process as herein described, the product comprising also a wettable additive incorporated therein, said wettable additive being capable of imparting a degree of wettability to the sheet product.

The wettable additive is preferably, although not necessarily, an inorganic material, conveniently a refractory material, and should have stability appropriate to the conditions of use. Thus, if the product is employed as an electrochemical cell diaphragm it is important that the wettable additive is chemically stable in the cell environment, that it is not leached too rapidly, if at all, from the diaphragm, and that its presence does not affect the performance of the diaphragm disadvantageously. It is also obviously important that the presence of the wettable additive should not weaken the diaphragm to such an extent that handling or use of the diaphragm is made unduly difficult or that the dimensional stability of the diaphragm is effected to an undesirable degree. The preferred wettable additive is an inorganic oxide or hydroxide, and examples of such materials are oxides and hydroxides of zirconium, titanium, chromium, magnesium and calcium, although any other suitable material or mixtures of such materials with those already mentioned may be employed.

The wettable additive may be incorporated in the spinning liquid either as such or as a precursor which may be converted by suitable treatment either during or after fibre spinning. The wettable additive may conveniently be present as a dispersed particulate material in suspension in the spinning liquid or alternatively it may be used in solution in the spinning liquid. For example we have successfully employed zirconium acetate as a dissolved component of the spinning liquid in appropriate concentration, the salt being converted to the oxide by sintering the sheet product which is produced.

It is sometimes found that, possibly because of adsorption of one component of the spinning liquid upon another, the use of dispersions of certain wettable additives does not give optimum results. In such circumstances we have found it advantageous to use coated particulate wettable additive, e.g. BTP 'Tioxide' grade RCR 2 or RTC 4, so that such adsorption is reduced. Alternatively the spinning liquid and a fibreizable solution or suspension of the wettable additive may be spun from different spinning points, conveniently in close proximity, to the same collector so that the resulting PTFE and additive fibres intermingle. As an example, fibreizable zirconium acetate solutions may be prepared by dissolving the equivalent of 20—35% by weight, preferably 25—32% by weight of zirconia in water to which is added high molecular weight linear organic polymer as described above for the preparation of the spinning liquid containing fluorine-containing polymeric material, the viscosity of the spinning liquid being adjusted to between 0.5 and 50 poise, preferably 1 and 10 poise.

Where the wettable additive is incorporated

as a precursor which is converted into the wettable additive by a post fibreization or post-impregnation treatment, the treatment employed should, of course, be one which is compatible with the production of a useful product and does not affect the properties of the product to an unacceptable degree. The choice of the wettable additive and its method of incorporation will be made in the light of this requirement.

Another method of incorporating the wettable additive, or a precursor, into the product is to apply it as a solid particulate material to the sheet product as it is being laid down upon the former. Conveniently this may be done by blowing the powder on to the product in a stream of air.

Wettable additive may be incorporated into the product after its formation, for example by immersing or steeping the product in a suspension or solution containing the wettable additive or a precursor of the wettable additive in a suitable liquid, followed by draining off of excess suspension or solution. A method of imparting water wettability to a sheet product is to contact the sheet product with a suspension of titanium dioxide in alcohol for several hours. The suspension is suitably agitated.

Suitable proportions of the wettable additive in the additive-containing sheet product are 5% to 60%, preferably 10% to 50%, by weight although the skilled man will have no difficulty in determining appropriate concentrations by a process of simple trial.

A further method of imparting water wettability to the product is to form hydrophilic groups on the fluorine-containing polymeric material in the product, for example by grafting of a suitable monomer or polymer, e.g. by radiation grafting.

The invention further provides a method of varying the porosity of a porous fluorine-containing polymeric sheet product by compressing a previously prepared porous sheet of the product to the desired porosity.

Compression is effected conveniently by placing the porous sheet product between platens and applying pressure in an appropriate direction so that reduction of the thickness of the sheet occurs until the degree of porosity (determined by trial) is attained.

We have sometimes found it useful to heat the sheet product during compression, and occasionally increased dimensional stability may be obtained by heating the sheet after compression.

Where wettable additive is to be incorporated into the sheet product by immersion as hereinbefore described compression and (optionally) heating it may precede or follow said immersion and drying of the impregnated sheet.

The use of elevated temperatures during the compression step is advantageous in facilitating compression, reducing to some extent the pressure required to attain a desired degree of porosity. Conveniently the sheet product is heated, during compression, to a temperature within the range 25°C to a temperature just below, e.g. about 25°C below, the softening point of the fluorine-containing polymeric material. For polytetrafluoroethylene the temperature is preferably between 100°C and 200°C.

Temperatures above the softening point of the fluorine-containing polymeric material may be employed, but not so high that complete collapse of the sheet occurs, with consequent complete loss of porosity, and it is desirable to control compression, whether carried out at temperatures above or below the softening point of the fluorine-containing polymeric material, so that complete collapse of the material is avoided, unless this is specifically required.

The degree of compression will depend upon the intended use of the sheet, but we have found that a reduction in thickness to 30 to 80%, usually 40 to 65% of its newly spun thickness is often appropriate.

Shaping of the sheet may also be effected during the compression step, for example by employing platens the faces of which comprise shaping means, e.g. raised and depressed regions whereby a contoured compressed sheet may be obtained or a sheet compressed in some areas and not, or less so, in others. In this way, for example, percolation of the electrolyte through different regions of an electrochemical cell diaphragm may be controlled by preparing a diaphragm having lower porosity in some areas e.g. where hydrostatic pressure in the cell is higher. Some relaxation of the compressed sheet product tends to occur gradually after compression, but this may be determined by simple experiment and appropriate conditions selected accordingly so that the relaxation is compensated for. By the application of post-formation compression techniques it is possible to prepare sheet products having a degree of porosity suited to a particular end-use and some increase in the strength of the sheet compared with the uncompressed mat may also be observed.

Sheet products made according to the invention find particular application as electrochemical cell diaphragms, since they may be highly chemically resistant. Although the following examples describe the production only of flat porous sheets, it will be appreciated that porous sheet products which are not flat may readily be made e.g. by deposition of the fibres upon a suitably contoured electrode from which they may be removed before or after sintering, depending upon the strength of the material and the degree of distortion tolerable in its removal. For example, the sheet product may be made in the form of a sleeve or tube by forming the sheet on a

tubular or cylindrical electrode. Dimensions of the sheet products will, of course, be governed by their intended use.

Alternatively the fibres could be spun on to an appropriately charged collector which is itself an electrochemical cell cathode gauze.

Alternative collectors are shown in Figures 2 and 3 in which 9 is a flat charge wire mesh or grill and 11 is a porous polyurethane sleeve over a charged rotating metal core 10.

Figure 4 shows diagrammatically, in side elevation, the compression of a polytetrafluoroethylene film sheet 20 to reduce its thickness by passing it between rollers 21 and 22, compression being followed by a heating step e.g. by radiant heaters 23. Diaphragms obtained by the process of the invention are particularly advantageous in that the material of which they are composed may be joined to itself or other materials, e.g. metals used as anodes and cathodes, or to cements used for example in cell construction, by the application of pressure and heat or by use of suitable inorganic or organic resin adhesives, for example epoxy, polyesters, polymethyl methacrylate and fluorinated thermoplastic polymers, for example fluorinated ethylene/propylene copolymers and PFA.

Other components may also be incorporated into the sheet product e.g. by inclusion of the component in the spinning liquid and co-spinning with the fluorine-containing polymeric material, or by spinning separately, or by post-treatment with a solution of suspension of the component, or by spraying the component onto the sheet product as it is being formed. Such components include asbestos fibrils of appropriate dimensions and ion-exchange materials e.g. zeolites, zirconium phosphates etc., whereby the properties of the resulting sheet may be modified.

It is possible also to employ the sheet products of the invention by subjecting them after formation to a comminution treatment whereby they are reduced to convenient dimensions for further processing, which may include admixture with, e.g. asbestos fibres or fibrils, zirconium oxide fibres etc. Said further processing could include formation by suitable shaping or forming techniques, including for example 'paper-making' or compression moulding technology, into desired shaped products, e.g. electrochemical cell diaphragms.

The invention is illustrated by the following examples:

Example 1.

The apparatus employed was as shown in Figure 1, the belt was of "Terylene" net 20 cm wide.

The spinning liquid was prepared by mixing 80 parts by weight of an aqueous polytetrafluoroethylene dispersion containing 60% by weight of polytetrafluoroethylene and containing 2% based on the weight of polytetrafluoroethylene of Triton X 100 surfactant ('Triton' is a Registered Trade Mark) (Rohm and Haas) with 20 parts by weight of a 10% by weight solution of polyethylene oxide "Polyox" WSRN 3000 in water ("Polyox" is a Registered Trade Mark). The polytetrafluoroethylene had a number average mean particle size of 0.22 micron and a standard specific gravity of 2.190. The surfactant may be any of the range capable of stabilising polytetrafluoroethylene dispersions of which Triton X 100 and "Triton DN65" are examples. The spinning liquid was spun from twenty 1 ml syringes on to the net situated 20 cm from the earthed needle tips, the charge on the roller being 20 Kv −ve.

The fibres were deposited over a width of about 16 cm and a sheet 0.4 mm thick was obtained. This sheet was then removed, placed on a stainless steel gauze support and sintered at 360°C for 5 minutes. A tough, porous, white, slightly rough sheet of uniform thickness was produced, consisting of fibres of average diameter 2—3 microns apparently bonded together into a reticulum having 78% free volume.

Example 2.

A sheet obtained as described in Example 1 was treated as follows with

(a) a 10% by weight aqueous solution of sodium hydroxide at 18°C for 24 hours,
(b) 10% by weight aqueous solution of hydrochloric acid at 18°C for 24 hours,
(c) a 10% by weight aqueous solution of sodium dihydrogen phosphate at the boil for 1 hour, and finally with
(d) a constantly agitated 10% by weight suspension of titanium dioxide (average particle size 0.2 micron) in isopropyl alcohol for 5 hours.

The polytetrafluoroethylene sheet impregnated with the titanium dioxide was washed with isopropyl alcohol to remove excess solid and then mounted in a vertical diaphragm cell for the electrolysis of sodium chloride.

Example 3.

A diaphragm was prepared by electrostatic spinning of a mix containing an aqueous dispersion of polytetrafluoroethylene of number average median particle size 0.22 microns (the Standard Specific Gravity of the polymer by ASTM test D 792—50 being 2.190) containing 3.6% by weight, based on the weight of the dispersion of surfactant "Triton" X100 (Rohm and Haas) and having a polytetrafluoroethylene solids content of 60% by weight and to which had been added, as a 10% by weight aqueous solution, 2% by weight of 4×10^6 molecular weight poly(ethylene oxide) (Union Carbide, "Polyox" grade WSRN 3000). The mix was fed at a rate of 1 ml/needle/h to a bank of 10 needles.

which was transversed parallel to the axis of a rotating drum collector/electrode over the entire length of the drum. The electrode potential was 20KV and the needle-electrode separation was 13cm.

Approximately 40 mls of mix were spun before the sheet was removed from the drum and sintered by placing on a stainless steel gauze in an oven at 380°C for 20 mins. The porosity of the sheet (% free volume or pore volume) was determined from the mean thickness area and weight of the sheet and from the density of polytetrafluoroethylene (2.13 g/cc). The mean thickness was 2.0 mm the porosity was 76%.

The sheet was then soaked for 2 days in an agitated 5% by weight dispersion of TiO_2 (BTP 'Trioxide' RCR3) in iso-propyl alcohol (IPA). When mounted in a 120 cm² vertical test cell for the electrolysis of brine the diaphragm yielded a cell voltage of 7.50 V at a load of 1.67 KAM^{-2} and at a permeability of 590 h^{-1}.

Example 4.

A sheet was spun as described in Example 1, except that every sixth syringe contained aqueous zirconium acetate in an amount equivalent to 28% by weight zirconia and 0.9% by weight of "Polyox" WRSN 3000. Collection and sintering were as described in Example 1 and a cream coloured porous sheet was obtained having good water wettability. Scanning electron microscope photographs showed the presence of 1 to 2 micron diameter "zirconia" fibres among those of polytetrafluoroethylene.

Example 5.

A mixture of 20 parts by weight of zirconium acetate spinning solution (see Example 4) and 80 parts by weight of polytetrafluoroethylene (see Example 1) was prepared and spun as before. The sheet product was cream in colour and had good water wettability.

Example 6.

To 99 parts by weight of the spinning liquid used in Example 1 was added 1 part by weight of potassium chloride. After spinning as described in Example 1, except that a wider net was used, a sheet 30 cm wide was obtained which after heating at 360°C for 5 minutes yielded a tough, white, very smooth sheet having fibre diameters in the range 0.5 to 1.5 microns and 60% free volume.

Example 7.

Samples of sheet produced by the process of Example 1 were pressed for a period of 3 minutes between metal plates at varying pressures and temperatures with the following results:—

Pressure (psi)	Temp °C	Porosity (% free volume)
0	20	78
1,470	180	20
4,410	180	2
2,240	20	42
5,000	20	20
20,000	20	16

Relaxation of the sheets so obtained occurred gradually as follows.

Porosity (%) Free volume:

Initial	After pressing	After 24 hours	After 3 days
78	42	52	56
77	54	57	70

Stabilisation of the compressed sheets was obtained by heating the sheets for 3 minutes at 380°C after pressing. The results were as follows:—

Initial porosity	After Pressing	After Heating	After 3 days
75	44	61	61

Example 8.

Two spinning liquids were spun and the sheet products were sintered as described in Example 3 but throughout spinning TiO_2 powder was deposited via an air stream on to the collecting drum. The TiO_2 content was controlled by the feed rate into the air stream. Both samples were pressed at approximately 100 psi for 3 mins at 100°C and subsequently heated for 15 mins at 380°C. The sheets were mounted in electrochemical cells as described in Example 3 from which the following results were obtained:—

Porosity	Thickness	TiO_2 content	Permeability	Voltage
41%	0.3 mm	8%	103 h^{-1}	3.45
50%	0.55 mm	35%	58 h^{-1}	3.30

Load	Time on Load	CE	CV
$2KAM^{-2}$	19 days	78.2%	76.8%
$2KAM^{-2}$	39 days	80.3%	59.2%

CE is the % current efficiency as standardised for diaphragm cells for the electrolysis of brine.

CV is the weight % measure of the amount of brine converted into useful product. Optimum values for this are around 50%.

Example 9.

Two samples of spinning liquid were spun and resultant sheet products sintered as described in Example 3, a bank of six needles was used. In the first case one of the six needles was fed with a zirconium acetate spinning solution and in the second case the zirconium acetate solution was fed to two needles. Polytetrafluoroethylene spinning liquid as used in Example 3 was supplied to the remaining needles. The zirconium acetate spinning solution contained an equivalent of 22% by weight of zirconia, 3% by weight of 2×10^5 and 0.5% by weight of 3×10^6 molecular weight poly(ethylene oxide). As a result of the dilute nature of the zirconium acetate spinning solutions and the approx 50% weight loss of these fibres on firing to zirconia, they were used only as an additional wetting agent and TiO_2 powder was blown into both sheets in the manner described in Example 8.

The polytetrafluoroethylene fibres were sintered and the zirconium acetate fibres were fired to an insoluble zirconia by heating for 30 mins at 380°C. Both samples were pressed to a load of 750 psi for 3 mins at 100°C followed by heating at 380°C for 10 mins. The following results were obtained from the diaphragms when mounted in the electrochemical cells described in the previous examples.

Porosity	Thickness	%TiO_2 (wt)	%ZrO_2 * (Vol)	Volts
56.8%	0.5 mm	26.4%	5.9%	4.75
46.0%	0.6 mm	40.0%	2.7%	3.50

Load	Time on load	Permeability	CE	CV
$2KAM^{-2}$	3 days	197 h^{-1}	97.4	22.2
$2KAM^{-2}$	27 days	83 h^{-1}	79.7	76.2

* This figure represents the volume of ZrO_2 fibres as a proportion of the total volume of the diaphragm.

Example 10.

A series of sheet products suitable for use as diaphragms in electrochemical cells was prepared from spinning liquids made up as described in example 3 but containing 4% by weight of a 2×10^5 molecular weight poly-

(ethylene oxide) (Union Carbide "Polyox" WSRN 80) added as a 25% by weight aqueous solution to the spinning liquid. Electrode voltage was 30 KV with a needle-electrode separation of 15 cm and feed-rates of 1.5—2.5 ml/needle/h. The needle-bank was traversed directly below the rotating drum electrode so that the fibres were spun upwards. Sheets were sintered on beds of fine TiO_2 powder to allow free movement of the sheets during the area shrinkage which accompanies sintering. By varying the volume of liquid spun, and by pressing to pre-set thicknesses, a range of diaphragms were produced with various thicknesses and porosities.

The sheets were thoroughly wetted by first soaking for a minimum of 2 hours in isopropyl alcohol and the sheets were then treated by soaking for 30 mins in solutions of tetra-butyl titanate in isopropyl alcohol. Finally, the sheets were immersed in water to hydrolyse the tetra-butyl titanate causing precipitation of colloidal TiO_2 on the surfaces of the PTFE fibres. The results obtained from the tests in the electrochemical cells are given in the following Table 1.

Example 11.

Using the techniques described in example 10 sheets suitable for use as diaphragms in electrochemical cells and having various porosities and thicknesses were prepared. However, in these sheets a range of TiO_2 loadings were incorporated into the fibres by spinning from co-dispersions of polytetrafluoroethylene and TiO_2. 60% by weight TiO_2 dispersions were prepared by high-speed mixing of TiO_2 powder (BTP "Tioxide" RCR2) in water containing 0.4% of "Calgon S" (Albright and Wilson de-flocculating agent) by weight of TiO_2 (Calgon is a Registered Trade Mark). Dispersed particle diameters were 0.4—0.5 μm. This dispersion was then added in appropriate amounts to the polytetrafluoroethylene dispersion used in the previous examples. The required quantity of poly(ethylene oxide) solution was then blended into the co-dispersion and the resulting spinning liquid was degased and filtered. We have found that higher concentrations and greater molecular weights of poly(ethylene oxide) are required in these co-dispersions as compared with normal pure polytetrafluoroethylene spinning liquid. In the results tabulated in the following Table 2 the concentrations and molecular weights quoted gave best spinning properties and fibres in the diameter range 0.8—1.8 μm.

Th results for each diaphragm are given and were obtained from the test electrochemical cells described in earlier examples. In each case the Load (current density) was $2KAM^{-2}$.

Example 12.

A polytetrafluoroethylene porous sheet prepared by the method described in example 4 was subjected to high energy radiation in the presence of acrylic acid which effected grafting of poly (acrylic acid) to the PTFE fibre surfaces.

The treated samples showed a 5% weight increase over the original sheet. When mounted in a standard test electrochemical cell as used in previous examples the diaphragm exhibited the following characteristics:—

Porosity	Thickness	Permeability	Volts	Load
51%	0.8 mm	57 h^{-1}	3.50	$2KAM^{-2}$

Days on Load	CE	CV
34	93.3%	53.4%

TABLE 1

Porosity	Thickness	Concentration of Tetra-Butyl Titanate Solution (Weight %)	Permeability	Volts	Load	Days on Load	CE	CV
71%	0.6 mm	25%	$427h^{-1}$	3.16	$2KAM^{-2}$	23	97.2%	35.6%
51%	0.5 mm	15%	86^{-1}	3.80	$2KAM^{-2}$	17	89.0%	42.7%
43%	0.7 mm	15%	$81h^{-1}$	3.40	$2KAM^{-2}$	19	92.8%	49.7%
75%	0.6 mm	10%	$209h^{-1}$	3.12	$2KAM^{-2}$	12	95.0%	40.9%
44%	0.46 mm	5%	$179h^{-1}$	3.30	$2KAM^{-2}$	6	88.8%	42.6%
52%	0.5 mm	5%	$97h^{-1}$	3.55	$2KAM^{-2}$	5	91.8%	43.9%
60%	0.5 mm	5%	$416h^{-1}$	3.30	$2KAM^{-2}$	7	91.5%	44.6%
82%	1.05 mm	5%	$411h^{-1}$	3.50	$2KAM^{-2}$	47	97.7%	41.4%

TABLE 2

"Polyox" Molecular Weight Mn	"Polyox" Concentration (Weight %)	TiO_2 (Weight %)	Porosity	Thickness	Permeability	Volts	Days on Load	% CE	%CV
2×10^5	4%	10%	68.0%	0.80 mm	$154h^{-1}$	5.05	2	87.9	47.5
2×10^5	5%	30%	69.0%	0.50 mm	$359h^{-1}$	3.65	3	92.7	45.9
4×10^5	2.5%	40%	53.0%	0.48 mm	$280h^{-1}$	3.35	9	83.6	53.5
4×10^5	3.5%	50%	64.0%	0.40 mm	$897h^{-1}$	3.20	21	92.1	40.4
4×10^5	3.0%	50%	83.7%	0.87 mm	$687h^{-1}$	3.30	63	94.3	43.3
4×10^5	3.5%	60%	87.4%	0.97 mm	$417h^{-1}$	3.25	34	86.7	40.9

WHAT WE CLAIM IS:—

1. A method of preparing a porous fluorine-containing polymeric sheet product which method comprises the steps of introducing an electrically-conducting spinning liquid comprising a fluorine-containing polymeric material into an electric field whereby fibres are drawn from the liquid to an electrode and collecting the fibres so produced upon the electrode in the form of a sheet.

2. A method according to claim 1 in which the polymeric material is polytetrafluoroethylene.

3. A method according to claim 1 or claim 2 in which the fibres are 0.1 to 25 microns in diameter.

4. A method according to claim 3 in which the fibres are 0.5 to 10 microns in diameter.

5. A method according to claim 4 in which the fibres are 1 to 5 microns in diameter.

6. A method according to any one of claims 1 to 5 in which the spinning liquid has a viscosity between 0.1 and 150 poise.

7. A method according to claim 6 in which the spinning liquid has a viscosity between 0.5 and 50 poise.

8. A method according to claim 7 in which the spinning liquid has a viscosity between 1 and 10 poise.

9. A method according to any one of the preceding claims in which the spinning liquid comprises an additional polymeric component which acts to enhance the viscosity of the spinning liquid.

10. A method according to claim 10 in which the additional polymeric component is selected from the group consisting of polyethylene oxide, polyvinyl alcohol and polyvinyl pyrrolidone.

11. A method according to claim 9 or claim 10 in which the additional polymeric component is present in the spinning liquid at a concentration within the range 0.01 to 8% by weight of the spinning liquid.

12. A method according to any one of the preceding claims in which the spinning

liquid has an electrical conductivity within the range 1 to 10^{-6} Siemens cm^{-1} to 5×10^{-2} Siemens cm^{-1}.

13. A method according to any one of the preceding claims in which the spinning liquid contains an electrolyte.

14. A method according to claim 13 in which the electrolyte is a salt present in a concentration within the range 0.2 to 3% by weight of the spinning liquid.

15. A method according to any one of the preceding claims in which a wettable additive is incorporated in the porous sheet product.

16. A method according to claim 15 in which the wettable additive is an inorganic material.

17. A method according to claim 16 in which the wettable additive is an inorganic oxide or hydroxide.

18. A method according to claim 17 in which the additive is an oxide or hydroxide of zirconium, titanium, chromium, magnesium or calcium.

19. A method according to any one of claims 15 to 18 in which the additive is included, either as the additive or as a precursor thereof, in the spinning liquid.

20. A method according to any one of claims 15 to 18 in which the additive is incorporated into the sheet product after formation of the sheet product.

21. A method according to claim 20 in which the additive is incorporated in the sheet product by immersing or steeping the product in a suspension or solution containing the wettable additive or a precursor of the wettable additive.

22. A method according to claim 20 in which the wettable additive is applied to the sheet product as a solid particulate material.

23. A method as claimed in any one of claims 15 to 22 in which 5% to 60% of wettable additive is incorporated into the sheet by weight of the additive-containing sheet product.

24. A method according to any one of the preceding claims in which the sheet product is subjected to compression whereby its thickness is reduced.

25. A method according to claim 24 in which the product is heated during or following compression.

26. A method according to claim 25 in which the heating is effected at a temperature within the range 25°C to 25°C below the softening point of the fluorine-containing polymeric material.

27. A method according to any one of the preceding claims in which the product is sintered after its formation.

28. A method according to any one of the preceding claims in which, subsequent to formation, the product is comminuted and reformed into a shaped product.

29. A method according to claim 1 substantially as hereinbefore described with reference to any one of Examples 1 to 12.

30. A porous fluorine-containing polymeric sheet product obtained by the method of any one of claims 1 to 29.

31. A product according to claim 30 which contains a wettable additive.

32. A product according to claim 30 or claim 31 in which the fluorine-containing polymer is tetrafluoroethylene.

33. A product according to any one of claims 30 to 32 in which the fibres are 0.1 to 25 microns in diameter.

34. A product according to any one of claims 31 to 33 in which the wettable additive is an oxide or hydroxide of zirconium, titanium, chromium, magnesium or calcium.

35. A product according to any one of claims 31 to 34 in which the concentration of wettable additive in the product is within the range 5 to 60% by weight of the additive-containing product.

36. A product according to claim 30 substantially as hereinbefore described with reference to any one of Examples 1 to 12.

37. A product according to any one of claims 30 to 35 which is suitable for use as a diaphragm in an electrochemical cell.

38. An electrochemical cell comprising a product according to claim 37.

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1522605 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

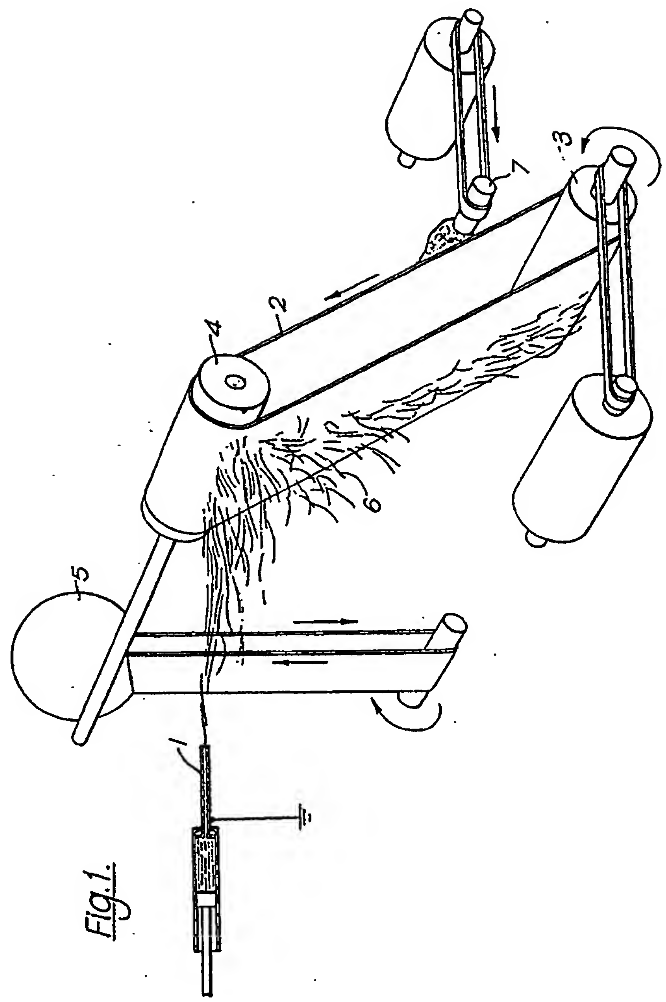

Fig.1.

Fig. 2.

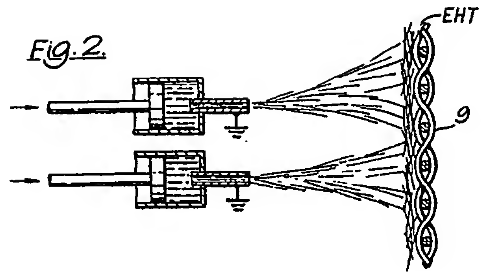

Fig. 3.

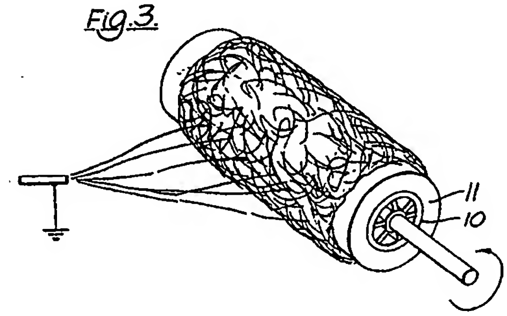

Fig. 4.